Dynamics of Epitaxy on the Nano-sized Semiconductor Surfaces

Principal Investigator: Deng-Sung Lin, Professor of Physics

Institution: Institute of Physics and Department of Materials Science and
                Engineering, National Chiao-Tung University
Mailing address: 1001 Ta-Hsueh Road, Hsinchu 300, TAIWAN
Phone: +886-3-5731994   FAX: +886-3-5720728
e-mail address: dslin@mail.nctu.edu.tw

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14. ABSTRACT

Semiconductor self assembled quantum dots (QDs) have emerged as one of the simplest subjects for exploring and exploiting the physics and device applications of charge carriers and excitons in the three dimensional confinement regime. Nanoscale-sized surface in the form of mesa or ridges on patterned substrates offer opportunities not only for creating large densities of QDs with great homogeneity but also for novel growth-control engineering. This project aims at a fundamental understanding of the size-dependent crystal growth phenomena during the formation of QDs on the surfaces of Si stripe and mesa strutures. Employing variable-temperature scanning probe microscope (VT-SPM) on the patterned substrates, we plan to observe in situ the atomistic chemical vapor deposition (CVD) growth mechanism of the QDs on the top terraces as well as on the sidewalls of pre-patterned structures. The key objective in this proposed research is to fabricate patterned structures with well-defined side walls. Specifically, we plan to fabricate patterned mesa and stripe structure with the flat (111) sidewalls on the Si(100) substrates by means of lithography and anisotropic wet chemical etch. When the patterned surface consists only of low-index surfaces with well-characterized structures, its growth behavior become more predictable and tunable. We will then perform epitaxy on the patterned surfaces and observe their evolution in atomic structure and in surface morphology on both the (100) top terraces and (111) sidewalls and QD formation in situ, in real time and in real space using VT-SPM. The fundamental understanding of the results could provide useful physical guidelines in preparing QDs for many researchers and contribute to device application development in a long-term base.

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Abstract

Semiconductor self assembled quantum dots (QDs) have emerged as one of the simplest subjects for exploring and exploiting the physics and device applications of charge carriers and excitons in the three dimensional confinement regime. Nanoscale-sized surface in the form of mesa or ridges on patterned substrates offer opportunities not only for creating large densities of QDs with great homogeneity but also for novel growth-control engineering. This project aims at a fundamental understanding of the size-dependent crystal growth phenomena during the formation of QDs on the surfaces of Si stripe and mesa strutures. Employing variable-temperature scanning probe microscope (VT-SPM) on the patterned substrates, we plan to observe *in situ* the atomistic chemical vapor deposition (CVD) growth mechanism of the QDs on the top terraces as well as on the sidewalls of pre-patterned structures.

The key objective in this proposed research is to fabricate patterned structures with well-defined side walls. Specifically, we plan to fabricate patterned mesa and stripe structure with the flat (111) sidewalls on the Si(100) substrates by means of lithography and anisotropic wet chemical etch. When the patterned surface consists only of low-index surfaces with well-characterized structures, its growth behavior become more predictable and tunable. We will then perform epitaxy on the patterned surfaces and observe their evolution in atomic structure and in surface morphology on both the (100) top terraces and (111) sidewalls and QD formation *in situ*, in real time and in real space using VT-SPM. The fundamental understanding of the results could provide useful physical guidelines in preparing QDs for many researchers and contribute to device application development in a long-term base.

I. Introduction and Motivation

Quantum dots (QDs) have sizes in the nanometer ranges, which is on the order of the electron wavelength. The spatial confinement of charge carriers in QDs leads to the quantization of the carrier energy levels. Thus, semiconductor quantum dots ~QDs provide a convenient means of exploring the physics of zero dimensional quantum confined systems. Inherently, the electronic and photonic properties of these quantized states depend strongly on the size of these QDs. Thus, the characteristics and properties of QD devices can be tuned by controlling the QDs' dimensions and relative positions. For example, optoelectronic devices based on quantum dot structures have demonstrated their high optical efficiency.[1] These promising features make QDs and QD arrays to be one of the most fascinating areas of semiconductor physics over the last decade.[2]

Long-range spatially order QDs are typically preferred in many electronic and optoelectronic devices. To this end, a variety of techniques can be used to fabricate QDs. More recently, there has been increasing interest in the study of self-organized quantum dot formation by selective growth on patterned substrates.[3,4,5,6] For example, several groups have fabricated self-assembled quantum dots such as InAs with molecular-beam epitaxy on 2D ordered mesa lattices with size of >250 nm. Long-range ordering of self-assembled Ge QDs nucleated on a limited surface area with nanometer dimensions had also been produced. These developments of the selective growth of QDs on the arrays of pre-patterned, finite sized surfaces were aimed to improve position, lateral coupling, and density control. These studies also indicate that epitaxy on the nanoscale-sized, even micron-sized semiconductor surfaces is different from that on the traditional surfaces. For example, Brakely *et al*. demonstrated that homoepitaxy on the Si(111) and Si(100) surfaces can create large step-free regions via a step flow process.[7,8]

The modified growth behavior on the nanoscale-sized surfaces in the form of mesa or ridges offers opportunities for creating novel thin film growth control. Namely, stains in the system, confined by the geometry, can exhibit modified growth dynamics and kinetics, and thus the growth dynamics and kinetics of the system can be size-dependent and thereby tunable. Jin *et al.*[9] determined the existence of tensile strain near the periphery of the Si mesa and compressive strain at the center, leading to Ge nucleation along the edges.[10] Vescan *et al.* found the lateral ordering of Ge islands on Si mesa edges is driven by the presence of tensile strain at the periphery of the mesas.[3] Yang, Liu, and Lagally showed that a surface chemical potential arisen from the stain relaxation can be used to control ordering in heteroepitaxy.[11]

To obtain better control the formation of QDs on the patterned substrates, further study on the growth kinetics and dynamics is necessary. So far, the growth behavior on the nanoscale-sized surfaces had been mostly examined on the QD's systems *ex situ* before and after the growth has been performed. This traditional way of study, *i.e.*, exemine-after-growth, often overlooks the initial stage of the growth processes, which might be essential for fully understanding the growth proccesses. Based on our extensive experence in real-time and real space study of chemical vapor deposition, we therefore propose to observe the kinetics and dynamics of thin films and QD growth on the nanoscale-sized surfaces.

II. Approach

This project aims at a fundamental understanding of the size-dependent phenomena during the growth of quantum dots on the surfaces of Si mesa strutures. The key objective is observe the growth of QDs *in situ*, in real time and in real space. We propose to fabricate mesa of vaious sizes on the Si(100) surfaces, to perform epitaxy on the patterned nanoscale-sized surfaces, and to image the growing nano-structure with variable-temperature ultra-high -acuum scaning probe microscopy (VT-UHV-SPM)).

IIA. Prevous work on real-time observation of chemical vapor deposition

Our group had extensice experence of imaging the chemical vapor deposition using VT-UHV-STM as shown in our publication list of five most relavent papers. We have been studying the physics of group IV semiconductor surfaces and thin films. The systems we had worked on before include the adsorption and growth of Si, Ge, P and B on the silicon and germanium surfaces.

One example is our previous study on Si homoepitaxy on the Si(100) surface. Figures 1 displays the CVD growth sequence at 490 °C, a temperature near the H_2 desorption peak. The evolution of the surface morphology during the growth shows that 2D epitaxial islands can grow larger in size and the island density is smaller. Nevertheless, ideal layer-by-layer growth does not occur. The second layer growth starts before the first layer completes growth. Further growth leads to increased roughness.

Figure 2 illustrates the UHV-CVD homoepitaxial growth experiment at 600 °C. In that study, the surface is exposed to disilane($\sim 2 \times 10^{-8}$ torr) for various duration as indicated. Prior to the gas exposure, an area with three-dimensional (3D) clusters appearing at the upper right corner is located for the experiment. The clusters are used as a marker and the largest 3D island measures ~9 Å in height. As the exposure increases, the 3D clusters are gradually buried by the grown film. After 100 L of disilane exposure, only a small bump less than 1 Å in height can still be found at the end, indicating that a film of ~6 ML thick is grown.

Figures 3, taken at 800 K, illustrates the typical growth behavior of P on the Si(100) surface in the temperature range of 800-900 K. Above 800 K, H desorbs immediately upon phosphine adsorption and dissociation and, in such a case, the surface coverage of H is nearly zero. The net effect is continuous phosphorus deposition until the entire surface is eventually passivated. At the temperature range of 800-900 K, the adsorbed P and/or displaced Si adatoms left behind after H desorption are mobile enough to reach the step edges, leading to step-flow growth. P is substantially lower in apparent height than Si. If only adsorbed P were responsible for the step flow, the growth areas at the step edge would appear darker than the terraces before growth. However, all areas in Fig. 9 appear the same, indicating that the chemical composition is about the same all over the surface, and suggesting that the growth of P proceeds by a steady increase in the proportion of P throughout the entire surface. At low coverage, most of the P atoms are expected to displace Si atoms on the terrace before traveling far. The ejected Si diffuses on the surface and eventually is incorporated into step edges. This scenario closely resembles the Si homoepitaxy. As the phosphine dosage increases, phosphorus accumulates and very anisotropic 2D islands begin to form on the terraces, as are shown in the images.
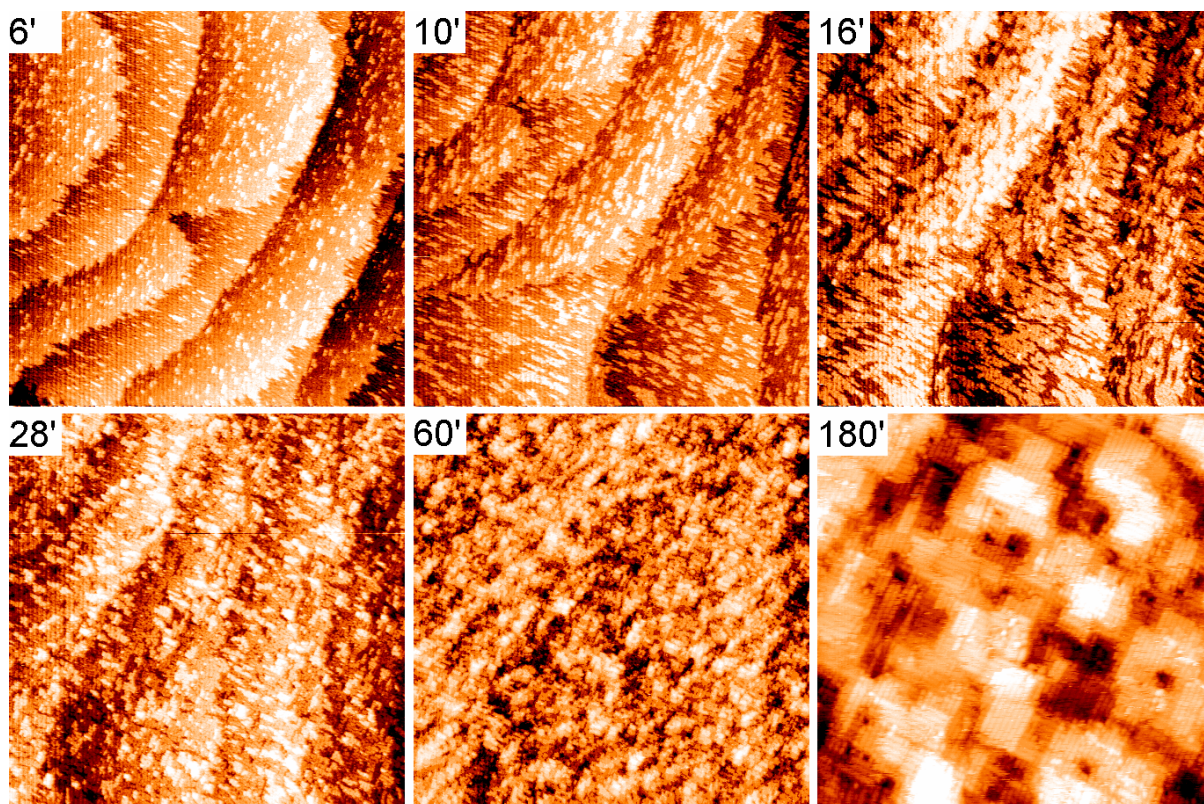
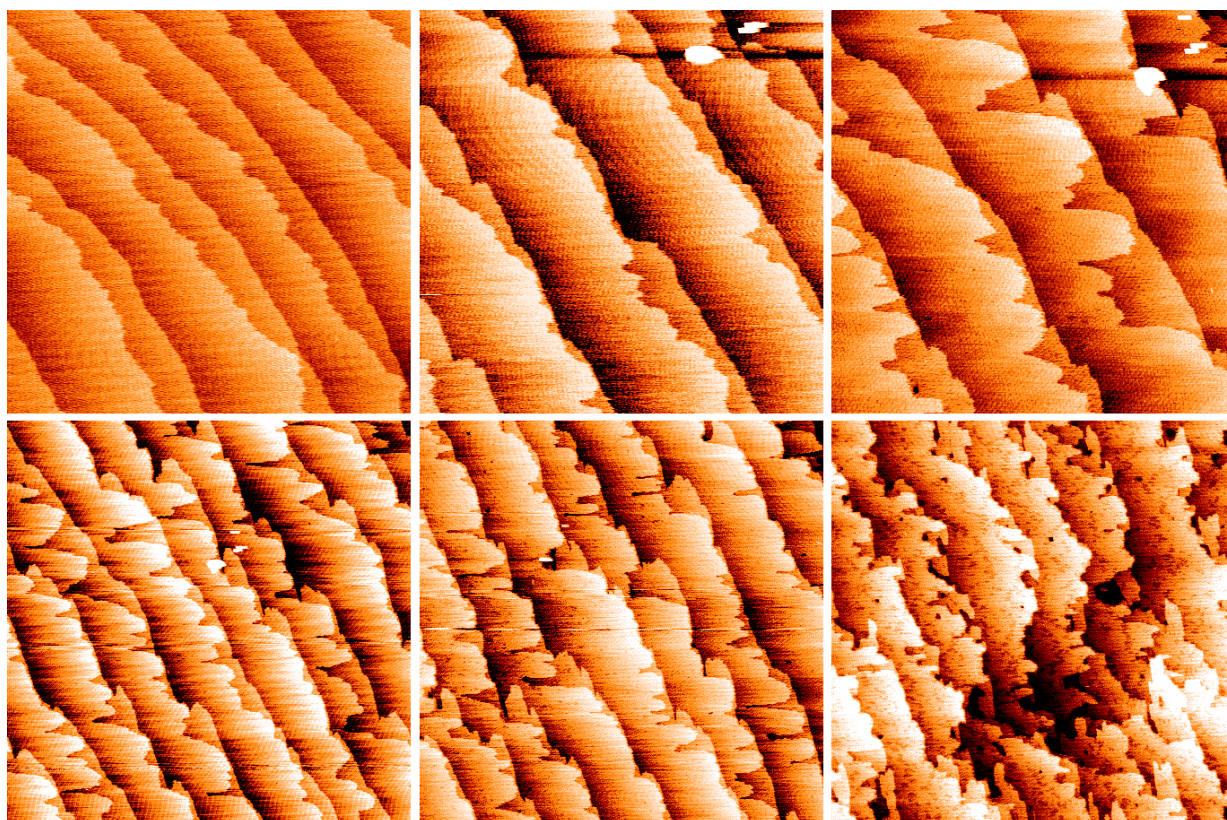Fig. 1. Real-time STM images (5000X5000 Å^2) of a growth sequence of Si on Si(100)-(2x1) at 490 °C.

Fig. 2. Real-time STM images of a growth sequence of Si on Si(100)-(2x1) at 600 °C. The images are of size 5000x5000 Å^2.
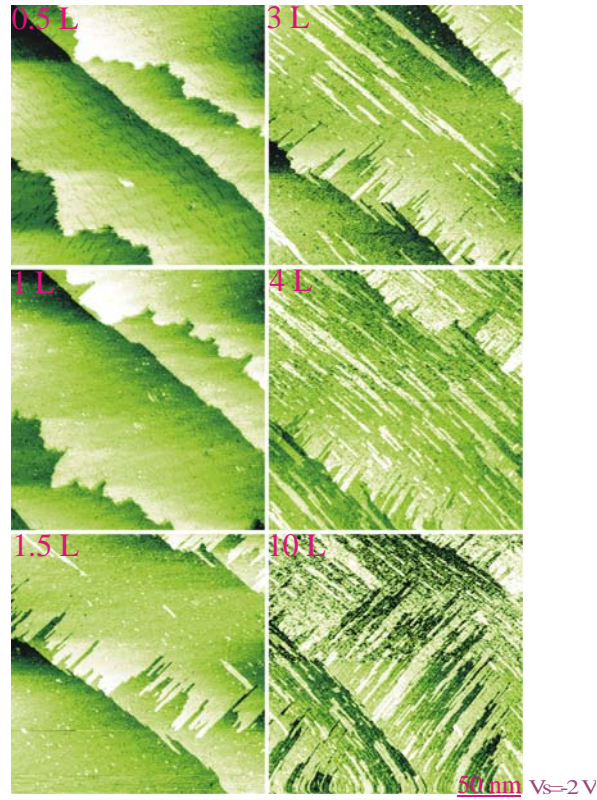
5

Fig. 3. Real-time STM images (2,000x2,000 Å^2) of Si(100) dosed by (a) 0.5, (b) 1, (c) 1.5, (d) 3, (e) 4, and (f) 10 L of phosphine at 800 K. The sample bias was -2 V; the tunneling current was 0.3 nA.

IIB. Preparation of nano-sized surfaces with well-defined sidewalls by anisotropic etching

Si mesa structures have been demonstrated to be an excellent template for studying homoepitaxy and heteroepitaxy phenomena. Brakely *et al*. produced two-dimensional periodic mesa and ridged structures on single crystal silicon as a starting pattern. They patterned various sizes (5-75 μm) of square ridge structures and observed the annealing effects on electromigration, point defects, and sublimation pits with an *ex situ* atomic force microscope (AFM). They demonstrated that arrays of step-free regions on the Si(111) and Si(100) surfaces can be created by annealing or homoepitaxy.[8] Stripes[12] with sizes in submicrons and crossed stripes[11] with sizes of ~2 μm had also been fabricated on the Si(100) substrates via holographic and conventional photolithography, respectively, for growing self-assembly of Ge QDs. Different conditions of local surface strains effect the preference of QDs on the sidewalls, or on the top terrace, or in the convex surface regions.

We would like to prepare patterns of mesa, stripe, and cross stripe structure on the Si(100) surfaces with (111) sidewalls by means of anisothropic wet etching. The angle between the (100) and the (111) planes is about 54°. To produce square or stripe top surface areas, previous studies typically employed reactive ion etching to create trenches with perpendicular side walls, leading to perpendicular sidewalls around the top surfaces. The sharp edges between the top terraces and their walls are inherently difficult to be imaged by STM. The straight edges often become more rounded after high-temperature annealing and the sidewall's surface structure is not well defined. Thus, interpretation of

the QD's growth mechanism at the sidewalls or on the top terraces, or between their boundary areas might become less evident.

The etch of monocrystalline silicon wafers along preferential directions is a typical process step in the fabrication of micromechanical devices in recent years. [13] The anisotropy is obtained through the different etch rates that selected chemicals exhibit against different crystalline planes.[14] In silicon, the atoms laying on (111) planes appear more densely packed than those on the (110) and (100) planes. As a consequence, certain etching formulations are favored in removing atoms from (110) and (100) planes. This result in the possibility of making V- or U-shaped structures, through an etch-resistant mask layer, which is usually made of silicon dioxide or nitride. A popular anisotropic wet etching bath is obtained with a solution of 40% in weight of potassium hydroxide (KOH) in isopropyl-alcohol. Alternatively, a different mix recipe: 50g KOH in 100g H_2O + 40 g (30 ml) of methyl-alcohol, is employed. Figure 4 shows a schematic of the etched structure with top (100) terrace and (111) sidewalls.
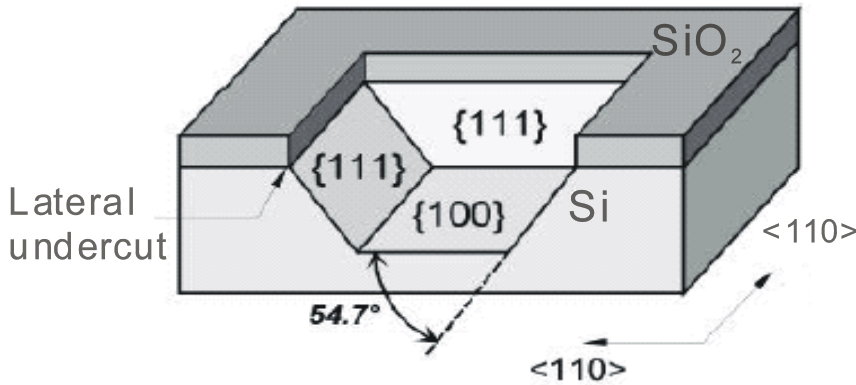

Fig. 4. Schematic diagram showing an inverted pyramid on the Si(100) surface with four side walls of (111) planes.

IIC. Imaging the growing thin films and QDs on the terraces and sidewalls

Our VT-UHV AFM/STM system, as shown in Fig. 5, is ultra-high vacuum compatible and allows chemical vapor deposition and molecular beam epitaxy of various materials. Therefore, we are able to study the growth phenomena occurred on the limited surface areas *in situ* at an atomic scale. As described in Sec. IIA, we have been studying the physics of group IV semiconductor surfaces and thin film growth of Si, Ge, and P on silicon and germanium surfaces. Recently, we are also able to acquire atomic resolved non-contact AFM images of ultra-thin oxide surfaces as displayed in Fig. 6. This ability enables us to image in sequence a) the patterned structures with the oxide layer, (b) the same surface after partial and complete oxide removal at 800-1200 °C, and (c) the growth of thin films and QDs with chemical vapor source all *in situ*.

The top (100) terraces and the (111) sidewalls of silicon have very much different atomic structure and dangling bond density. During CVD, the sticking coefficients of source molecules on the two kind of surface are often quite different. Also, adatoms migrate at different rates on the two surfaces. If heteroepitaxy is involved, the two interfaces will exhibit different strain fields, too, owing

Fig. 5. Picture of the variable-temperature STM/AFM system in an ultra-high vacuum chamber capable of chemical vapor deposition.
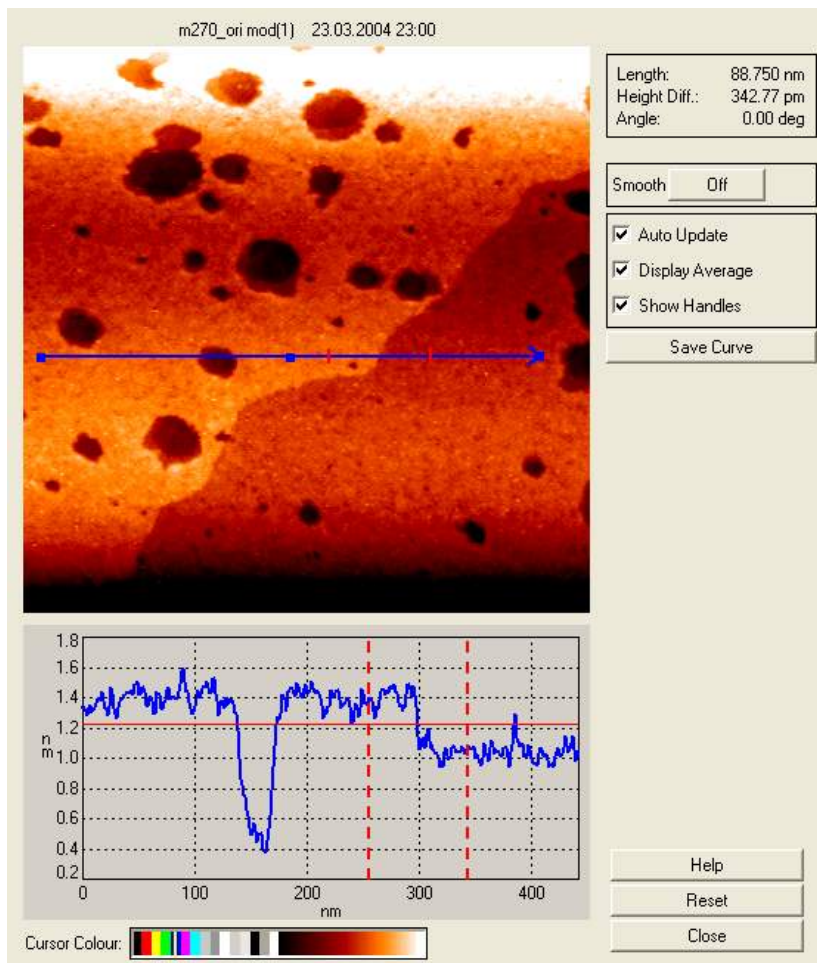

Fig. 6. Non-contact AFM image showing SiO_2 desorption crators on the SiO2/Si(111) surface. Frequency shift=-60 Hz
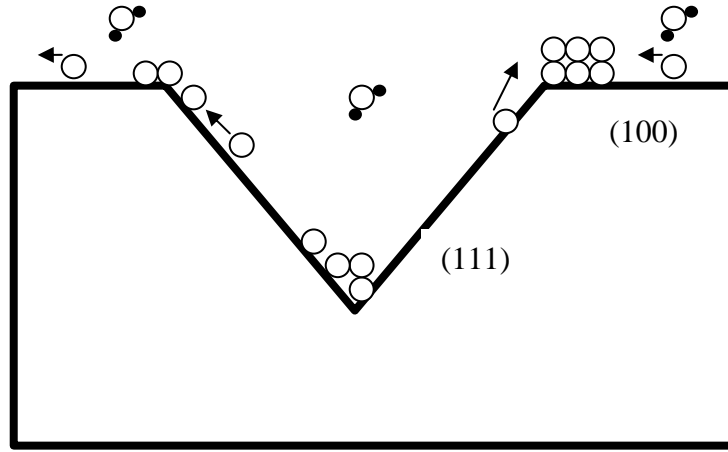
Fig. 7. Schematic diagram showing a side view of the Si(100) top terraces with the (111) sidewalls and deposited adatoms.

to different surface reconstruction. All these factors lead to different film deposition rates and QD formation density on the top terraces and the sidewalls, as illustrated in Fig. 7.

III. Pay-off

Many promising new device applications are based on self-assembly QD formation on the pre-patterned semiconductor substrates. In particular, optoelectronic devices based on quantum dot structures dots have demonstrated their high optical efficiency. Numerous groups are currently working on the better control of QD's density, size homogeneity and position ordering. Yet, the detailed, atomic-resolved, and *in-situ* observation of the self-assembly growth is still lacking. Although proven to be of importance in positioning the desired QDs,[12] the sidewalls on patterned structures in previous studies resulted from high temperature annealing and were not well-defined nor well-characterized.

This proposed research intends to fabricate patterned stripe and mesa structures with well-defined side walls. With the help of variable-temperature SPM on the patterned substrates, the atomistic CVD growth mechanism of QDs on the top terraces as well as on the sidewalls are to reveal the structure evolution of all surface areas on substrate and the very initial stage of QDs' formation. The fundamental understanding of the growth mechanism of QDs could provide in-depth physical guidelines for many researchers and contribute to device application development in a long-term base.

IV. Summary and Concluding Remarks

This proposal is a relatively more fundamental study of the growth, structure, and growth-control relationships of the finite-sized surfaces on single crystal materials. We plan to pattern mesa and stripe structure with flat (111) sidewalls on the Si(100) substrates by means of conventional photolithography and e-beam lithography followed by anisotropic wet chemical etch. The evolution of the surface structure on both the (100) top terraces and (111) sidewalls and QD formation during in situ chemical vapor deposition are to be observed in real time and in real space using VT-SPM. The sticking probability of the source molecules, the surface structure, and the growth modes are all

different on the (100) top terraces and (111) sidewalls, leading to possible new findings in the QD formation processes and control factors.

A critical step is to be able to fabricate a system with the desired top terraces and well-defined sidewalls, which will then allow us to investigate various kinetic and dynamic effects during the growth of QDs. Our fundamental research on the growth processes will be of useful for better tuning of QDs' growth parameters for electronic and optoelectronic device systems such as SiGe heterostructures. We expect that these experiments will work well. There might be problems due to unknown parameters, unfavorable experimental conditions, and unforeseen reasons. For examples, the pattern structure might change much during oxide removal at high temperatures. The scanning tunneling microscope might suffer reduction in its resolution on the (111) sidewalls since it tilts 55° away from the usual scanning plane. But the only way to find out is to try and try hard. We might even find interesting surprises.

IV. Budget

V. ACADEMIC VITAE

Deng-Sung Lin
Professor of Physics

Institute of Physics and Department of Materials Science and Engineering
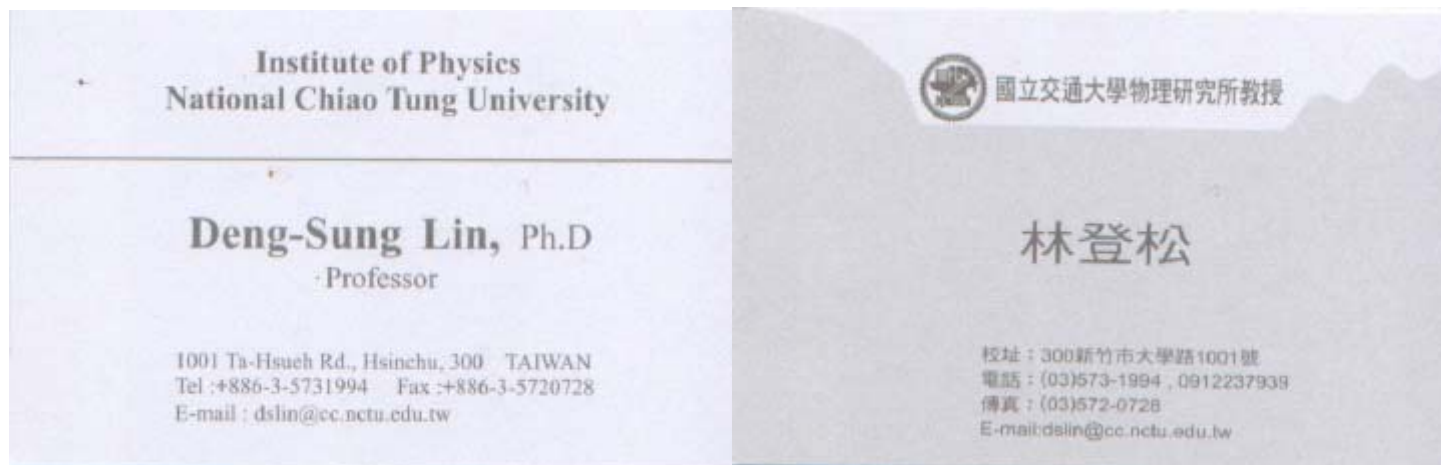National Chiao-Tung University
1001 Ta-Hsueh Road, Hsinchu 300, Taiwan
e-mail address: dslin@mail.nctu.edu.tw
Phone: +886-3-5731994   FAX: +886-3-5720728

PERSONAL DATA

- Date of Birth: March25, 1963

- Place of Birth: Taichung, TAIWAN

- Marital Status: Married, 2 daughters

- S.S. number: 477-11-2066

PROFESSIONAL EXPERIENCE

- Professor, Institute of Physics, National Chiao-Tung University, Taiwan (2000-)

-          Chairman, Institute of Physics, National Chiao-Tung University, Taiwan (2002 2004)

- Deputy Director, Center for Nano Science and Technology, National Chiao-Tung University (2004-)

- Visiting Scientist, Department of Physics, Cornell University, USA (March-August 1999)

- Associate Professor, Institute of Physics, National Chiao-Tung University, Taiwan (August 1994- July 2000)

- Postdoctoral Research Associate, Department of Physics, Univ. of Illinois at Urbana-Champaign, USA (1994)

- Instructor in Physics, Chinese Military Academy (1985- 1987)

EDUCATION

- University of Illinois at Urbana-Champaign, Illinois, USA, 1993; Ph. D., Physics

- National Taiwan University, Taipei, Taiwan, 1985; B.S., Physics

PUBLICATIONS (5+5)

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